

diameter and the cross-mark of the slider is set at the given value of f . The further procedure is obvious.

The combination I(a)+II does the same work as the machine devised by Evans & Peiser (1942). A disadvantage in comparison with that machine is that the computation is effected in two stages. On the other hand, the accuracy is much greater, and the speed of the operations is so high that it is doubtful whether the total

time of computation will be larger. Owing to the low price of the small calculating machines used, the whole arrangement will be cheap.

Reference

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The shape transform in electron diffraction by small crystals. By A. L. G. REES and J. A. SPINK, *Division of Industrial Chemistry, Commonwealth Scientific and Industrial Research Organization, Box 4331 G.P.O., Melbourne, Australia*

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In considering the diffraction of X-rays or electrons by a small crystal the reciprocal lattice cannot be regarded simply as a lattice of points of extent negligible compared with the dimensions of the reciprocal cell, but one must take into account the finite extent of the crystal and the shape of its boundary. This was first discussed in detail by v. Laue (1936), who demonstrated that, as a result, the scattering amplitude about each reciprocal-lattice point would be extended in directions normal to the boundary faces of the crystals. Ewald (1940) and Patterson (1939) have refined v. Laue's treatment by considering the reciprocal lattice as the Fourier transform of the density distribution in the crystal. This was conveniently expressed mathematically by the use of a shape function $s(u_i)$ of the co-ordinates u_i , having the value 1 inside, and 0 outside, the crystal boundary. If $\rho(u_i)$ is the density distribution in the finite crystal and $\rho_\infty(u_i)$ that in the perfectly periodic infinite crystal, then

$$\rho(u_i) = \rho_\infty(u_i) s(u_i).$$

The Fourier transform $S(\xi_i)$ of the shape function $s(u_i)$, expressed as a function of the reciprocal-space co-ordinates ξ_i , then determines the distribution of scattering amplitude around each reciprocal-lattice integer point. Patterson (1939) has calculated the shape transform for a number of regular polyhedra. Their form around each reciprocal-lattice integral point is characterized by a principal maximum centred on the point and subsidiary maxima whose magnitude and position are determined by the size and shape of the crystal.

Using a high-resolution electron-diffraction camera designed and constructed in this laboratory (Cowley & Rees, unpublished), we have succeeded in demonstrating the existence of these subsidiary maxima in the individual reflexions from small ZnO particles. These may be seen in the reproductions of individual reflexions on the $11\bar{2}0$ ring in Figs. 1 and 2. To our knowledge, no authentic experimental proof of the existence of subsidiary maxima, and therefore of the complete optical theory of electron diffraction, has previously been obtained. The particles of ZnO prepared by burning the metal in air are known from electron microscopy to be needles of diameter 100–500 Å, considerably elongated along $[0001]$; independent evidence from the refraction fine-structure in the same patterns (Rees & Spink, in preparation) suggests that these particles are either circular cylinders or hexagonal prisms with somewhat rounded edges. The shape transforms will therefore extend appreciably only in the re-

ciprocal-lattice plane normal to c^* , and the resulting diffractions will be streaked at angles determined by the orientation of the crystal with respect to the beam and the indices of the particular reflexion.

We have derived the shape transform (for the elongated hexagonal prism) along two relevant directions. For the $[1\bar{1}00]$ direction it is of the form

$$\frac{4}{3} \left[\frac{\sin p}{p} + \frac{1 - \cos p}{p^2} \right],$$

and for $[1\bar{1}20]$, $\frac{4}{3} \left[\frac{\cos q - 2 \cos^2 q + 1}{q^2} \right].$

Examination of these two functions shows that the complete transform will have extensions of largest amplitude along the directions $[1\bar{1}00]$, $[10\bar{1}0]$ and $[01\bar{1}0]$ from each integer point of the reciprocal lattice; along other directions (e.g. $[11\bar{2}0]$) the subsidiary maxima will decrease in amplitude very rapidly with distance from the integer point. For the circular cylinder, Patterson (1939) has shown that the shape transform is of the form $2J_1(p)/p$ for the direction $[h.k.\bar{h}+k.0]$, where $J_1(p)$ is the first-order Bessel function. For the elongated cylinder the transform may be pictured as a family of concentric tores lying in a plane normal to c^* . The properties of these transforms (for example, the positions of the maxima and zeroes) may be used to distinguish between the two possible crystal habits; also the separation of the subsidiary maxima may be used to obtain the crystal dimensions. The greatest diameter of the needle giving the reflexion indicated by the arrow in Fig. 1 is calculated to be 400 Å, a value consistent with electron-microscopic observation. Moreover, the spacings of the maxima and zeroes suggest that this crystal at least has a hexagonal rather than circular section.

The intensity distribution illustrated in Fig. 2 shows a pair of broad maxima symmetrically disposed about the Bragg position and distinct from the structure associated with the shape transform. This is the result of refraction of the electron beam passing through a crystal of hexagonal section. The coexistence of refraction and interference effects in the fine structure of these patterns complicates their interpretation, but leads one to expect that for cylindrical crystals the subsidiary maxima would be obscured, except for extremely narrow crystals having negligible absorption.

A small improvement in resolution will permit the use of electron diffraction for the unambiguous determination

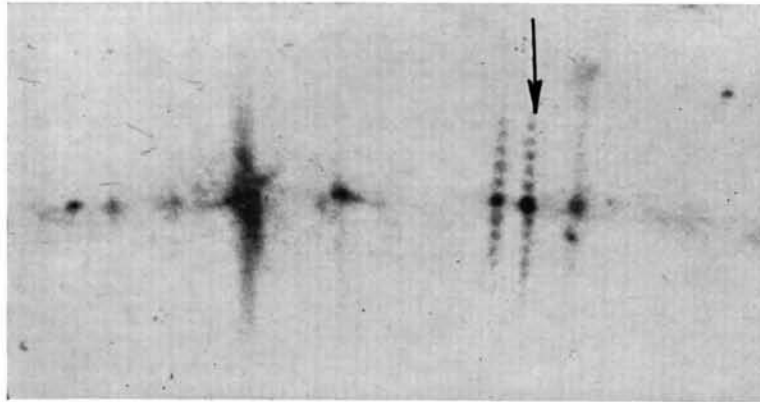


Fig. 1. Group of single-crystal reflexions on $11\bar{2}0$ ring of ZnO electron-diffraction pattern. Subsidiary maxima apparent in two instances.

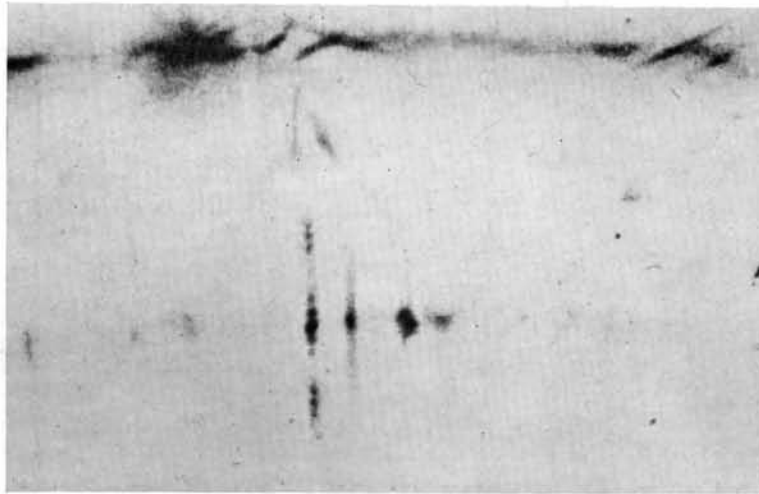


Fig. 2. Single-crystal reflexion on $11\bar{2}0$ ring showing refraction components and subsidiary maxima around each component.

of the shape and dimensions of small crystals. The method could be applied with profit to the study of the size and shape of molecularly dispersed protein molecules, particularly those, such as horse haemoglobin, whose intramolecular order is independent of water (Perutz, 1949).

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Preliminary X-ray investigation of nitrogen triphenyl and phosphorus triphenyl. By E. R. HOWELLS,*
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1. Single-crystal X-ray measurements

Nitrogen triphenyl crystallizes in plates bounded by (100) and (100), with prominent inclined (101), (10 $\bar{1}$) and {110} faces, and minor {010}, (201), (001) and (00 $\bar{1}$) faces. Phosphorus triphenyl grows in crystals elongated along [001], bounded by {110} and terminated by {101} and {001}. Oscillation and rotation photographs about the principal crystallographic axes show that both compounds are monoclinic and have the unit-cell dimensions given in Table 1.

Phosphorus triphenyl exhibits absences in the reflexions $h0l$ when h is odd, so that the space group is either Pa or $P2/a$. The external form of the typical crystal suggests that the structure has a centre of symmetry, and the distributions of the intensities of reflexions $h0l$ and $hk0$ agree satisfactorily with the theoretical curve for a centrosymmetric projection (Howells, Phillips & Rogers, 1950). The space group is therefore more probably $P2/a$. Nitrogen triphenyl and phosphorus triphenyl are not isomorphous; in fact there is no isomorphous pair in the

Table 1. *Single-crystal data*

(Accuracy of cell dimensions about 1%; of monoclinic angle 0.5°.)

	a (A.)	b (A.)	c (A.)	β	No. of molecules per unit cell	Class	Space group
Nitrogen triphenyl	22.6	11.2	11.2	90°	8	Monoclinic hemihedral	Pm
Phosphorus triphenyl	11.6	15.1	8.57	93°	4	Monoclinic holohedral	$P2/a$

Table 2. *Powder photograph data*

Nitrogen triphenyl			Phosphorus triphenyl		
Interplanar spacing (A.)	Relative peak intensity	Indices	Interplanar spacing (A.)	Relative peak intensity	Indices
7.93	0.19	011, 210, 201	9.20	—	110
6.24	0.04	301, 310	8.62	0.30	001
5.61	0.21	020, 002, 400	7.64	0.39	020
4.93	0.43	220, 202, 401, 410	6.38	0.18	120
4.46	1.00	500, 302, 320	5.76	0.55	200
4.15	0.20	321, 312, 501, 510	4.90	0.80	201
3.93	0.36	022, 420, 402, 122	4.60	1.00	220, 130, 211
3.69	0.15	—	4.27	0.52	002
3.50	0.24	—	3.98	0.55	221
3.36	0.20	—	3.77	0.50	040, 022, 310
3.19	0.15	—	3.45	0.27	202, 311
2.97	0.06	—	3.28	0.11	032
2.84	0.10	—	3.08	0.09	222
2.76	—	—	2.86	0.11	400, 003, 232
2.69	—	—	2.75	0.09	113
2.48	—	—	2.66	0.18	023, 322
2.39	—	—			
2.28	—	—			
2.21	—	—			
2.07	0.04	—			

The X-ray reflexions with nitrogen triphenyl show no systematic absences; the space group is therefore one of $P2$, Pm , $P2/m$. From the external symmetry it seems that the most probable space group is Pm .

group composed of these compounds and the arsenic, antimony and bismuth triphenyls (Wetzel, 1942).

Patterson-Fourier syntheses have been performed for the projections of phosphorus triphenyl on (001) and (010). The intensities were estimated visually from zero-layer-line Weissenberg photographs. The first projection shows sharp peaks at (0, 0.416) and (0.500, 0.416); the

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